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EVALUATION OF THE COMPETITIVENESS OF HOUSEHOLD GLASSWARE DECORATED BY PLASMA SPRAYING

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The results of evaluating the competitiveness of glassware decorated by the plasma spraying method are discussed. The specifics of a method proposed for estimating the competitiveness is consideed.

One promising method for decorating household glassware is plasma spraying, i.e., deposition of melted glass particles on a glass article surface using a stencil. The main advantages of the plasma spraying method are the possibility of applying a decorating material with T_g exceeding the T_g of the substrate and elimination of the time-consuming and costly operation of annealing used to fix the decorative coating [1]. This suggested that glassware decorated by plasma spraying is competitive against glassware decorated by such traditional methods as painting, silk-screen printing, decalcomania, aerography, and filling.

To assess this competitiveness, we considered articles (wine and liqueur glasses and the like) produced at the Krasnyi Mai glass works that were decorated by plasma spraying or by the traditional methods.

First we evaluated the technical level of the articles that mostly depends on their reliability. The service reliability of glassware is an extremely important quality parameter determined by the service life, or durability, and the keeping quality [2]. The service life of glassware depends on the resistance of the decorative coating to the effect of the ambient environment in service and on the wear resistance of the product.

Glass articles in service are subjected to multiple thermal cycling (washing in cold and hot water). Abrupt temperature differences may impair the mechanical and aesthetic properties of the decorative coating up to destruction of the article and, therefore, may substantially lower its quality.

The main reasons for destruction of decorative coatings on glass products are the following:

– difference in the TCLE values of the decorate coating and the substrate;

– existence of temporary and constant stresses in the decorative coating;

– thermal aging of the decorative coating in thermal cycling.

However, the resistance of a decorative coating on household glass to the effect of the ambient medium is not included in the standard parameters regulating its consumer properties. We propose to include a parameter reflecting the resistance of a decorative coating on glassware to the ambient environment into the list of regulated consumer properties. It is recommended to assess the resistance of a decorative coating to the effect of the ambient medium (durability) based on the following parameters: heat resistance, water resistance, acid resistance, microhardness, and the strength of adhesion of the coating to the substrate.

The heat resistance of coatings was determined as follows. Glassware samples decorated by plasma spraying and by the traditional methods and having a temperature of 20 ± 1°C were consistently heated in a heating cabinet at temperatures ranging from 100 to 140°C. Then the articles were immersed in a vessel filled with water having a temperature of 15 ± 1°C. The thermal resistance of the decorative coating was inferred from the temperature difference at which the coating was destroyed or microcracks appeared in it.

The water resistance of decorative coatings was determined in accordance with GOST 10134.1, method A. According to the requirement of GOST 30407, the water resistance of household glassware cannot be lower than hydrolytic class IV.

The acid resistance of decorative coatings was determined according to GOST 30407. This standard implies testing in 4% acetic acid for 24 ± 0.5 h at a temperature not lower than 15°C. The products are regarded to be acid-resistant if the tested surface shows no boundaries caused by a loss of luster or a modification of the coating color. Conse-

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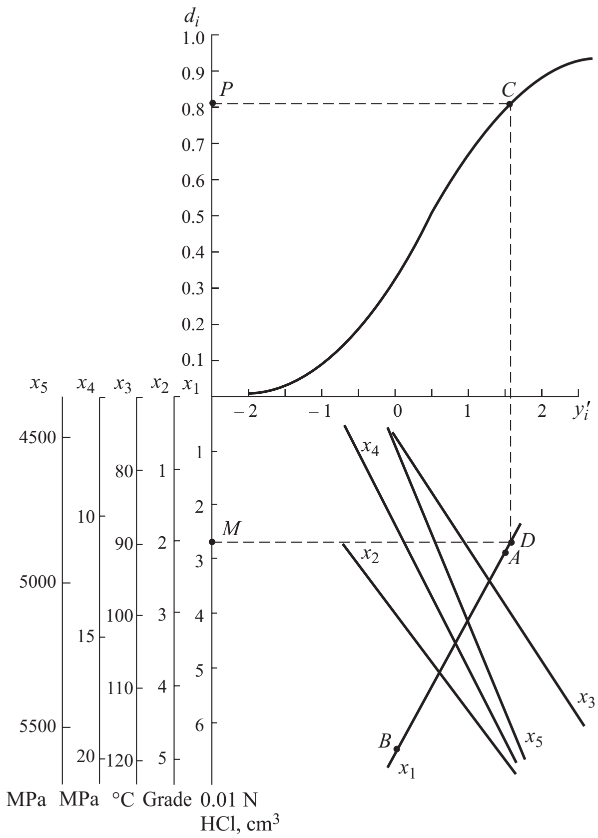

Fig. 1. Nomograms for determination of desirability indexes: x_1) water resistance; x_2) acid resistance; x_3) thermal resistance; x_4) adhesion strength; x_5) microhardness; d_i) partial desirability function; y_i) dimensionless quality index.

quently, the acid resistance of a decorative coating is assessed visually using a five-grade scale.

The microhardness was determined by the standard method [3] and the strength of adhesion of the decorative coating to the substrate was tested on a R-0.5 tensile-testing machine [4].

The absolute values of the properties of decorative coatings obtained by plasma spraying and the traditional methods are listed in Table 1.

TABLE 1

Decoration method	Properties of decorative coatings					
	water resistance		acid resistance, grade	thermal resistance Δt, °C	microhardness, MPa	adhesion strength, MPa
	hydrolytic class	quantity of 0.01 N HCl, cm^3				
Painting	IV	4.217	3	85	4797	11.98
Silk-screen printing	IV	3.266	4	93	5097	14.19
Decalcomania	IV	3.875	4	96	4904	10.02
Filling	III	2.762	5	109	5501	16.54
Aerography	IV	3.501	4	90	5197	15.01
Plasma spraying	III	2.657	5	122	5798	17.98

We performed an evaluation of the competitiveness of household glassware decorated by plasma spraying using the desirability scale reflecting the dependence of the desirability parameters d_i on the dimensionless parameters y_i, into which the dimensional quality parameters are converted. This dependence is described in the form of

$$d_i = \exp\left(-e^{-y_i}\right)$$

or

$$y' = -\ln(-\ln d_i) = a_0 + a_i y_i,$$

where d_i is the partial desirability function; y_i is the natural value of the individual quality parameter; y' is the dimensionless quality parameter; a_0 and a_i are coefficients depending on selecting the base values of individual quality parameters.

In order to obtain the desirability function, all measured characteristics of glass articles were converted into the dimensionless scale y_i. Conversion into dimensionless parameters was carried out using the Hompertz curve variety proposed for this purpose by Harrington [2], which establishes a relationship between the desirability index of an estimated property a_i and the dimensionless index y_i of this property (Fig. 1). It should be taken into account that the construction of the desirability scale is essentially a subjective process reflecting the opinion of a consumer or an expert regarding the individual parameters of the glass product quality.

The desirability scale was constructed using the quantitative estimate method. The desirability values interval is usually selected between 0 and 1. At $d = 0$, the value of a parameter is unacceptable, and $d = 1$ correlates with the optimum value of this parameter, when a further improvement of this parameter in the nearest future is impossible or not important.

Bound indexes of desirability taking into account quality grading

Quantitative value of the desirability scale	Desirability of the quality parameter value
0.80 – 1.00	Excellent
0.63 – 0.80	Good
0.37 – 0.63	Satisfactory
0.20 – 0.37	Bad
0.00 – 0.20	Very bad

According to the above scale, the following reference points were established: 0.37 is the value is below which the coating is considered unsatisfactory; 0.63 is the lower bound of good quality; 0.80 is the lower bound of excellent quality.

Based on an expert poll, in which researchers and experienced and qualified sales managers participated, a list of

TABLE 2

Grade	Hydrolytic class	Quantity of 0.01 N HCl used for titration, cm^3
Excellent	I	0.00 – 0.32
	II	0.32 – 0.65
	III	0.65 – 2.80
Satisfactory	IV	2.80 – 6.50
Bad	V	More than 6.50

TABLE 3

Grade	Quality evaluation	Organoleptic evaluation
5 – 4	Excellent	No changes in tint and luster
4 – 3	Good	Hardly noticeable changes in luster
3 – 2	Satisfactory	Hardly noticeable changes in luster and color
2 – 1	Bad	Perceptible changes in luster and color
1 – 0	Very bad	Significant changes in luster an color

properties was compiled and the weight coefficients of the parameters considered were determined.

Properties of decorative coating for glassware	Weight coefficient m_i
Water resistance	0.200
Acid resistance	0.196
Thermal resistance	0.220
Microhardness	0.188
Strength of adhesion of coating to the substrate	0.194

The limiting values for water resistance were determined taking into account the obligatory requirements of GOST 30407 and recommendations of the State Institute of Glass (GIS) [5]. The hydrolytic classification of glass based on the GIS method and its grading are shown in Table 2.

Glasses requiring not more than 6.50 cm^3 of 0.01 N HCl for titration belong to hydrolytic class IV and are regarded as "satisfactory." This is taken as the lower bound of an acceptable water resistance.

To convert the natural parameters into dimensionless indexes, it is necessary to solve a system of equations determining the coefficients a_0 and a_1 (Fig. 1):

$$\begin{cases} 0 = a_0 + a_1 y_{\text{bad}}; \\ 1.53 = a_0 + a_1 y_{\text{exc}}, \end{cases}$$

where y_{bad} and y_{exc} are the worst and the best reference values of the natural parameters.

To determine the desirability parameters d_i for water resistance, the coefficients a_0 and a_1 were calculated and equations for conversion to the dimensionless value y_i were composed:

$$\begin{cases} 0 = a_0 + 6.5a_1 & (a_0 = 2.691); \\ 1.53 = a_0 + 2.8a_1 & (a_1 = -0.414). \end{cases}$$

In this case $y_1 = 2.691 - 0.414x_1$.

We developed a scale for grading the acid resistance of a decorative coating using a five-grade scale (Table 3).

After solving the system of equations characterizing the acid resistance of a decorative coating, we obtain

$$\begin{cases} 0 = a_0 + 3a_1 & (a_0 = -2.295); \\ 1.53 = a_0 + 5a_1 & (a_1 = 0.765). \end{cases}$$

Then $y_2 = -2.295 + 0.765x_2$.

The minimal thermal shock that is withstood by the decorative coating without visible destruction and formation of microcracks, equal to 75°C, is the lower bound for estimating a glass article as "satisfactory." A glass article withstanding a temperature difference of 100°C is estimated as "excellent." After solving the system of equations characterizing the heat resistance of the decorative coating, we obtain

$$\begin{cases} 0 = a_0 + 75a_1 & (a_0 = -4.575); \\ 1.53 = a_0 + 100a_1 & (a_1 = 0.061). \end{cases}$$

In this case $y_3 = -4.575 + 0.061x_3$.

The dependences for the conversion of natural parameters into dimensionless indexes for microhardness ($y_4 = -6.855 + 0.0153x_4$) and strength of adhesion of a decorative coating to the substrate ($y_5 = -153 + 0.153x_5$) were obtained in the same way.

Using the desirability curve (Fig. 1) and the nomograms of water resistance, acid resistance, thermal resistance, microhardness, and strength of adhesion of a decorative coating to the substrate, the absolute values of these properties for the traditional decoration methods and the plasma spraying method were converted into dimensionless parameters. For instance, let us determine the desirability index d_i of a decorative coating obtained by plasma spraying using its water resistance equal to 2.57 cm^3 (0.01 N HCl used in titration). Using the desirability bounds taking into account the quality grading and the hydrolytic classification of glasses, let us mark point A (Fig. 1) with coordinates of $x_1 = 2.8$ and $y_1 = 1.53$ and point B with coordinates of $x_2 = 6.5$ and $y_2 = 0$. Point B is the lower bound of water resistance of decorative coatings in accordance with the hydrolytic classification recommended by GIS. Let us mark a straight line via points A and B, which expresses the relationship between y and x and has the form of $y_1 = 2.691 - 0.414x_1$.

To convert any dimensional parameter x (for instance, $x = 2.57\ cm^3$) into a dimensionless desirability index d, we construct a horizontal line via the point M on the axis x corresponding to the ordinate 2.57 up to intersection with the straight line AB. We draw a perpendicular from point D to the axis y and continue it to the point C of intersection with the desirability curve $d_i = f(y)$. Next, we draw a perpendicular from point C to the axis d and find the value of the desirability index (point P) $d = 0.83$. The dimensionless indexes of the properties of decorative coatings are represented in Table 4.

To determine the technical level of articles, the properties of decorative coatings were compared in pairs: painting — plasma spraying; silk-screen printing — plasma spraying,

TABLE 4

Properties of decorative coatings	Dimensionless property indexes of decorative coatings d_i						Relative property index of decorative coatings					Weight coefficient
	plasma spraying	painting	silk-screen printing	decalco-mania	filling	aerography	q_1	q_2	q_3	q_4	q_5	
Water resistance	0.83	0.67	0.78	0.72	0.81	0.76	1.24	1.07	1.15	1.03	1.09	0.200
Acid resistance	0.80	0.37	0.65	0.65	0.80	0.65	2.16	1.23	1.23	1.00	1.23	0.196
Thermal resistance	0.96	0.57	0.70	0.78	0.92	0.66	1.68	1.37	1.23	1.04	1.46	0.220
Microhardness	0.91	0.54	0.67	0.52	0.82	0.73	1.69	1.36	1.75	1.11	1.25	0.188
Strength of adhesion to substrate	0.81	0.48	0.57	0.37	0.78	0.61	1.69	1.42	2.19	1.04	1.33	0.194

TABLE 5

Decoration method	Integrated (complex) quality index Q	Production cost of decoration per unit C_i, rubles/piece	Economic index $I_i = C_{plasm}/C_0$	Competitiveness $K = Q/I_i$
Painting	1.686	1.71	0.169	9.976
Silk-screen printing	1.286	0.49	0.592	2.172
Decalcomania	1.494	0.77	0.376	3.973
Filling	1.039	1.02	0.284	3.658
Aerography	1.273	0.65	0.446	2.854
Plasma spraying	–	0.29	–	–

etc. The relative indexes of the properties of decorative coatings were calculated by the differential method.

For instance, the relative property indexes of painted and plasma-sprayed coatings were calculated using the dimensionless indexes of coating properties:

– water resistance of decoration $q_1 = 0.83 : 0.67 = 1.24$;

– acid resistance of decoration $q_2 = 0.80 : 0.37 = 2.16$.

Using the arithmetic mean of the relative property indexes, an integrated quality index (which characterizes the technical level of quality) of decorative coatings produced by plasma spraying was calculated [6]. An example of this is the calculation of the integrated quality index for household glassware decorated by plasma spraying and by painting:

$$Q_1 = \sum_{i=1}^{n} m_i q_i = (1.24 \times 0.2) + (2.16 \times 0.196) +$$
$$(1.68 \times 0.22) + (1.69 \times 0.188) + (1.69 \times 0.194) = 1.686,$$

where m_i is the respective weight coefficient of the properties and q_i is the relative quality index.

This index is greater than unity; consequently, decorative coatings produced by plasma spraying surpass coatings produced by the traditional methods. The results of the calculation of the integrated parameter are given in Table 5.

In the second phase the competitiveness of decorative coatings was calculated using the economic parameters [7]. The results of calculations of competitiveness are listed in Table 5. Since this competitiveness index is greater than 1, it can be stated that glass products decorated by plasma spaying are more competitive than glassware decorated by the traditional methods.

All this indicates that plasma spraying is a promising method for decorating glass articles and modifying the surface of various materials.

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